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Low-Temperature Process to Improve the Leakage Current of $(Ba, Sr)TiO_3$ Films on Pt/TiN/Ti/Si Substrates

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In this study, we employed an oxygen plasma post-treatment to improve the leakage characteristics of Pt/$(Ba, Sr)TiO_3$(BST)/Pt capacitors prepared by the RF cosputtering technique. Applying oxygen plasma treatment to BST thin films can effectively passivate the oxygen vacancies of the BST films, thus decreasing the electric conduction paths of leakage current. The leakage current is reduced by as many as two orders of magnitude by this low-temperature (250°C) and short duration (~5 min) process. However, the usage of oxygen plasma treatment is not unrestricted. Plasma treatment over a long time (more than 10 min) degrades the leakage characteristics, due to plasma damage. Therefore, a proper oxygen plasma treatment for as-deposited BST films is desired to improve leakage characteristics of BST thin films.

KEYWORDS: BST films, RF cosputtering, oxygen vacancies, O_2 plasma, low temperature

1. Introduction

Barium strontium titanate (BST) films with a high dielectric constant have attracted great attention for practical use in the capacitors of giga-era dynamic random-access memory (DRAM).[1–4] To satisfy gigabit (Gbit) generation requirements, BST films with considerably high dielectric constants are necessary to provide sufficient charge in a miniaturizing storage capacitor to maintain immunity against soft error[5] as well as keep the cell structure simple. Other basic requirements for BST thin films include features such as low leakage current, high breakdown electric field, high time-dependent dielectric breakdown (TDDB), and low fatigue and aging effects.[6,7]

One of the most crucial issues for electrical parameters has been the leakage current of DRAM cells. Once data have been written in DRAM, charges stored in each capacitor must maintain more than the critical amount of charges for a time interval (>DRAM refresh time) so that the information stored in each DRAM cell can be read out correctly. The operation voltage, V_{cc}, for Gbit DRAMs is about 2 V. The voltage difference between two electrodes of the DRAM capacitor is $1/2V_{cc}$ (1 V). The leakage current measured at 1 V for the above-mentioned BST thin films is recognized to be dominated by the Schottky emission (SE) (electrode-limited) conduction mechanism.[8–10] The SE leakage current can be affected by the metal work function of the electrodes, the oxygen vacancy accumulation at the electrode interface, and the surface morphology of the BST thin films.[11–14] The mechanism of leakage current has been ascribed to the variation of the oxygen vacancies in the BST thin films.[8–10,14–17] Recently, it was reported that the higher leakage current of BST films could be effectively reduced by activated oxygen annealing.[14,16,17] However, high processing temperatures (>500°C) and long process duration (~1 h) were necessary for these postannealing processes.

In this investigation, oxygen plasma treatment was performed on as-deposited BST films at a low substrate temperature (250°C) in order to passivate the oxygen vacancies. Applying oxygen plasma treatment can provide active oxygen atoms to decrease the oxygen vacancies and improve the quality of BST films. Plasma treatments with different time intervals are also used to examine their effects on the leakage characteristics of BST thin films. In addition, the mechanism of improvements in the leakage characteristics of BST films has been investigated via various characterizations.

2. Experimental

Figure 1 shows a cross-sectional scanning electron microscope (SEM) micrograph of the BST capacitor with 300°C-deposited BST films. The structure of Pt/BST/Pt/TiN/Ti/Si was employed to simulate the practical capacitor over a bit-line (COB) DRAM capacitor structure. After a standard Radio Corporation of America (RCA) cleaning process, Ti and TiN films with 50 and 100 nm thicknesses serving as the adhesion and the barrier layers, respectively, were sequentially deposited on the p-type Si(100) substrates by the sputtering technique. A 200-nm-thick Pt layer as the bottom electrode was also deposited by sputtering at room temperature. Accordingly, a Pt/TiN/Ti/Si substrate was pre-

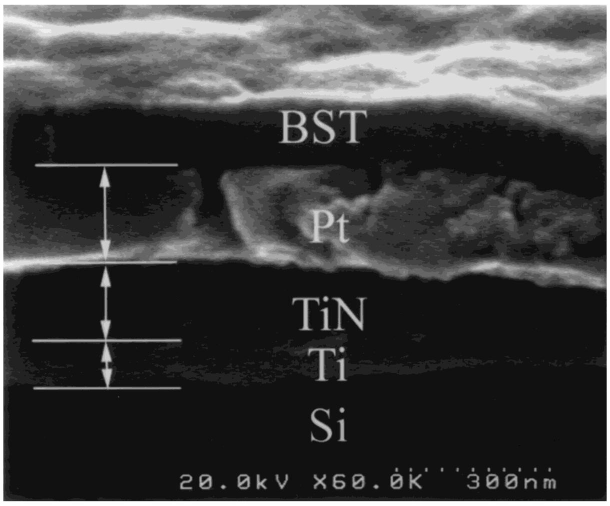

Fig. 1. Cross-sectional SEM micrograph of the BST/Pt/TiN/Ti/Si for which the BST was deposited at 300°C.

pared. $Ba_{0.5}Sr_{0.5}TiO_3$ films, all with a nominal thickness of 100 nm, were then deposited using a RF magnetron cosputter system at a substrate temperature of 300°C. To control the Ba/Sr ratio of BST thin films by tuning the RF power, $BaTiO_3$ and $SrTiO_3$ targets were used simultaneously. In order to achieve paraelectric characteristics, the Ba/Sr ratio of 1 : 1 was selected in this investigation. The RF powers for the deposition of $BaTiO_3$ and $SrTiO_3$ were 175 and 230 W, respectively.

After depositing BST films, the oxygen plasma post-treatment was performed on planar-type plasma in a 12-inch chamber for 3, 5, 10 and 15 min, to passivate the oxygen vacancies in various BST films. The operating conditions for the oxygen-plasma treatment are a flow rate of 900 sccm, a gas pressure of 650 mTorr, a substrate temperature of 250°C, and a RF power of 300 W. Finally, Pt top electrodes with a diameter of 150 μm were deposited on the BST films by sputtering via a metal shadow mask process.

The composition of the resultant $(Ba, Sr)TiO_3$ films were analyzed by Rutherford backscattering spectroscopy (RBS). The surface morphology, the cross-sectional view, and the film thickness of the BST films were examined by scanning electron microscopy (SEM). The crystallinity and grain size estimated from the Scherrer equation were characterized by a Siemens D5000 diffractometer.[18] In addition, the surface roughness was inspected using an atomic force microscope (AFM). An automatic measurement system was conducted to obtain the current–voltage (I–V) characteristics of the resultant BST capacitors.

3. Results and Discussion

Figure 2 presents the variation of the leakage current of as-deposited BST films with applied voltage. The leakage current under reverse bias is much higher than that under positive bias. The barrier height of SE is a function of the work function of the electrode metal, electron affinity of the dielectric, and the surface states. The Poole-Frenke (PF) transport mechanism (bulk limited) results from the lowering of the barrier height of traps in the dielectrics. Hence, the PF transport mechanism does not present polarity dependence.[8–10, 17] The higher reverse current shown in Fig. 2 indicates that the leakage current is dominated by the SE conduction mechanism rather than the PF transport mechanism. Since the material of the top electrode is the same as that of the bottom electrode, the higher reverse leakage current is likely due to the high concentration of oxygen vacancies at the interface with the top electrode.[8–10, 17] In order to enhance the crystallinity and step coverage of BST films deposited by sputtering, substrate heating is necessary. However, as the BST films were deposited at a high substrate temperature (>300°C), oxygen would escape and thus oxygen vacancies were generated according to:

$$O_0 \leftrightarrow V_0^{++} + 2e^- + 1/2O_2,$$

where O_0, V_0^{++} and e^- represent the oxygen ion at its normal site, oxygen vacancy and electron, respectively. A higher concentration of oxygen vacancies would give the BST materials n-type conductivity due to the electrons generated, causing larger leakage currents.

Since the oxygen vacancies generated during the film deposition process greatly affect the leakage characteristics, applying an oxygen plasma treatment can provide active oxygen atoms to decrease the oxygen vacancies and, furthermore, improve the quality of BST films. Figure 3 shows the dependence of the dielectric constant and the leakage current measured at various electric fields on O_2 plasma treatment with different time intervals after the BST film deposition. A considerable reduction of the leakage current is noted in the O_2 plasma-treated samples for 3, 5 and 10 min, especially that for 5 min. This improvement in leakage characteristic could be attributed to the compensation of oxygen vacancies near the surface or the improved surface roughness.[13, 14] Of these two possibilities, it was found that no obvious difference appeared in the surface roughness between the as-deposited BST films and that of samples with O_2 plasma treatment for 5 min. On the other hand, judging from the Auger electron spectroscopy (AES) profiles, the samples with oxygen plasma treatment exhibited a larger amount of oxygen in the BST films than the as-deposited specimen, as shown in Fig. 4. Therefore, the improvement of leakage current at negative bias is primarily attributed to the compensation of surface oxygen vacancies. Moreover, the leakage currents in the high electric field region (0.3, −0.3 and 0.5 MV/cm) are also improved. The leakage

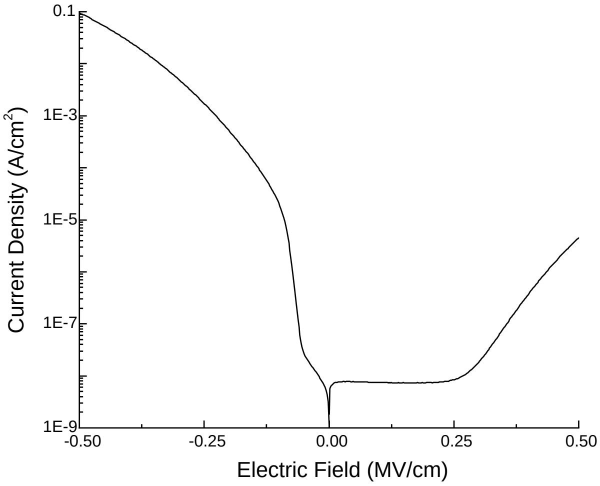

Fig. 2. Variation of leakage current of as-deposited BST films with applied voltage.

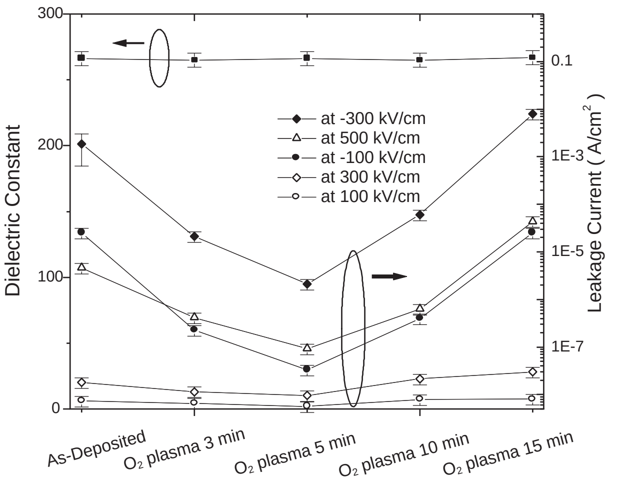

Fig. 3. Dependence of the dielectric constant and the leakage current measured at various electric fields with a delay time of 30 s on O_2 plasma treatment for different time intervals after the BST film deposition.

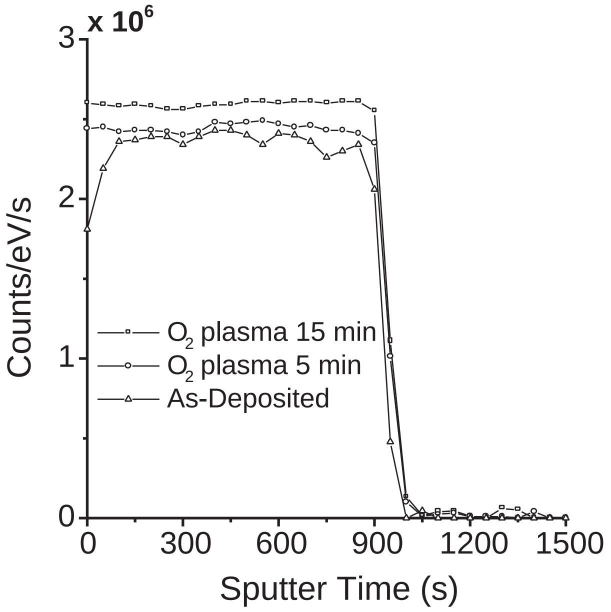

Fig. 4. AES profiles of the BST films without plasma post-treatment and with plasma post-treatment of 5 min, respectively.

mechanism in such a region is dominated by the PF transport mechanism.[8–10, 15–17] Accordingly, the oxygen plasma treatment can compensate the oxygen vacancies not only on the surface but also in the bulk. The oxygen radical in oxygen plasma is so active that it can oxidize BST film and compensate oxygen vacancies. However, for the samples with longer plasma treatment intervals of 10 and 15 min, the leakage current was degraded, especially in the case of the 15 min treatment, which is attributable to damage induced by plasma treatment over a long-time. The preferential crystal orientation of each BST film, as checked by X-Ray Diffraction Analysis (XRD), is (110). According to the Scherrer formula, the average grain size ($<$100 nm) can be estimated by

$$D = 0.9\lambda/(B^{*}\cos\theta),$$

where D is the grain size, λ is the X-ray wavelength ($\sim$0.15428 nm), B is the full-width at half-maximum (FWHM) of the XRD peak, and θ is the diffraction angle.[18] The FWHM of each sample analyzed by XRD is essentially identical, about 0.01725. The estimated grain size of each sample is therefore about 8.3 nm. This finding is consistent with our electrical measurements. There is no obvious difference in the dielectric constant of BST films with O_2 plasma treatment of various durations, as shown in Fig. 3. Hence, proper and careful oxygen plasma treatment should be carried out to effectively improve the leakage characteristics of BST thin films.

4. Conclusions

The composition of BST thin films fabricated by the RF sputtering technique shows serious oxygen deficiency, which greatly affects the leakage characteristics of the BST films. Applying oxygen plasma treatment to as-deposited BST films can effectively passivate the oxygen vacancies at low substrate temperatures and short process duration. Consequently, the plasma technique significantly improves the leakage currents as a result of the reduction of high-concentration oxygen vacancies of the as-deposited BST films. However, plasma treatment over a long time degrades the leakage characteristics of the BST films, due to plasma damage. Therefore, proper and careful oxygen plasma treatment, after depositing the BST films, should be employed to improve the leakage characteristics of BST thin films without degradation.

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